Development of High Performance LIB in Japan

For CO_2 Reduction from human society

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Energy & CO_2

- CO_2 emission from cars ?
- EV can reduce CO_2 emission or not ?
- Life Cycle Assessment (LCA) for CO_2 emission
- For LCA for Cars
  - Production of car
  - Driving of car
  - Recycle and destruction of car
- Fuel: Gasoline, Diesel, Electricity (from electric power plant or Natural energy)

Parameters for LCA Calculation

CO_2 emission from Fuels

Fuel or Electricity	CO_2 emission
Electricity	0.572 kg/kW h
Gasoline	2.69 kg/L
Diesel	2.85 kg/L
Solar Energy	0.03 kg/kW h

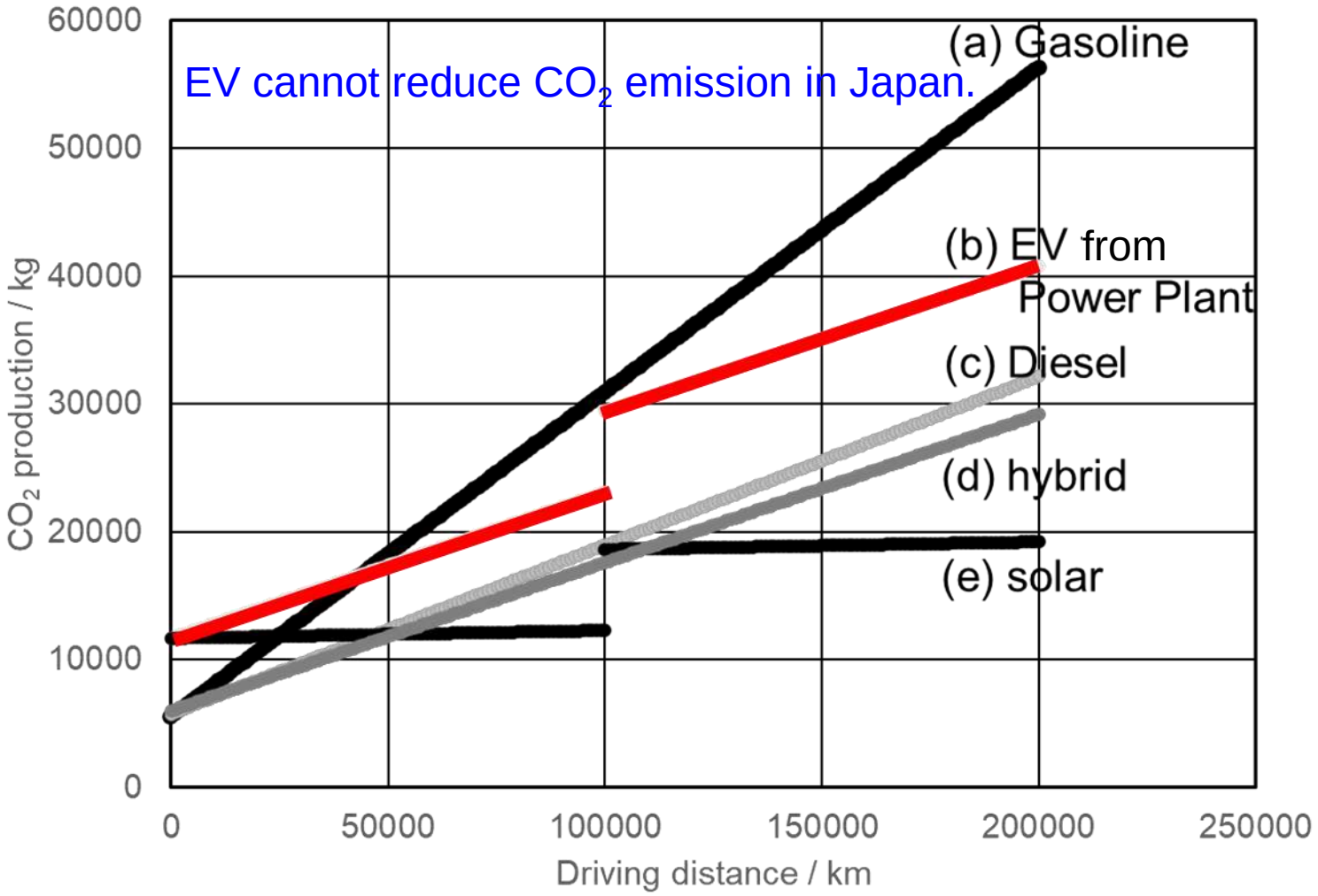
CO_2 Emission during driving & battery exchange

Car	New car Production	Fuel economy and Electric cost	CO_2 emission/km	Battery Exchange
Gasoline	5493 kg	10.6 km/L	0.254 kg	
Diesel	5758 kg	21.6 km/L	0.132 kg	
HV	6000 kg	23.6 km/L	0.116 kg	
EV	11681 kg	5.03 km/kW h	0.114 kg	6337 kg
EV (solar)	11681 kg	5.03 km/kW h	0.006 kg	6337 kg

CO_2 emission from 1 kW h

Country	CO_2 Emission / kg
Canada	0.151
U.S.A.	0.456
France	0.046
Germany	0.450
Italy	0.342
Spain	0.293
Sweden	0.011
U.K.	0.349
Russia	0.395
India	0.771
China	0.657
Korea	0.526
Japan	0.540

LCA (CO_2) for EV

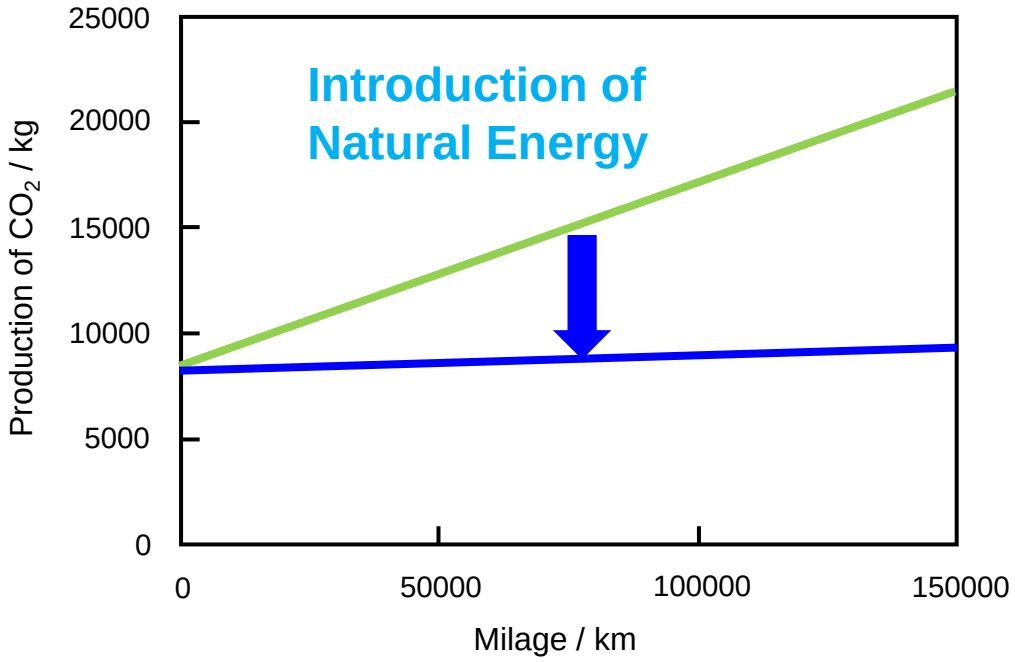


New Targets for LIB

- What kinds of characteristics of rechargeable battery have to be improved for EV application?

- Improvement of LCA by Long Cycle Life
- Reduction of Cost and Improvement of LCA by Higher Energy Density
- High Performance Battery for Introduction of Natural Energy

Introduction of Natural Energy



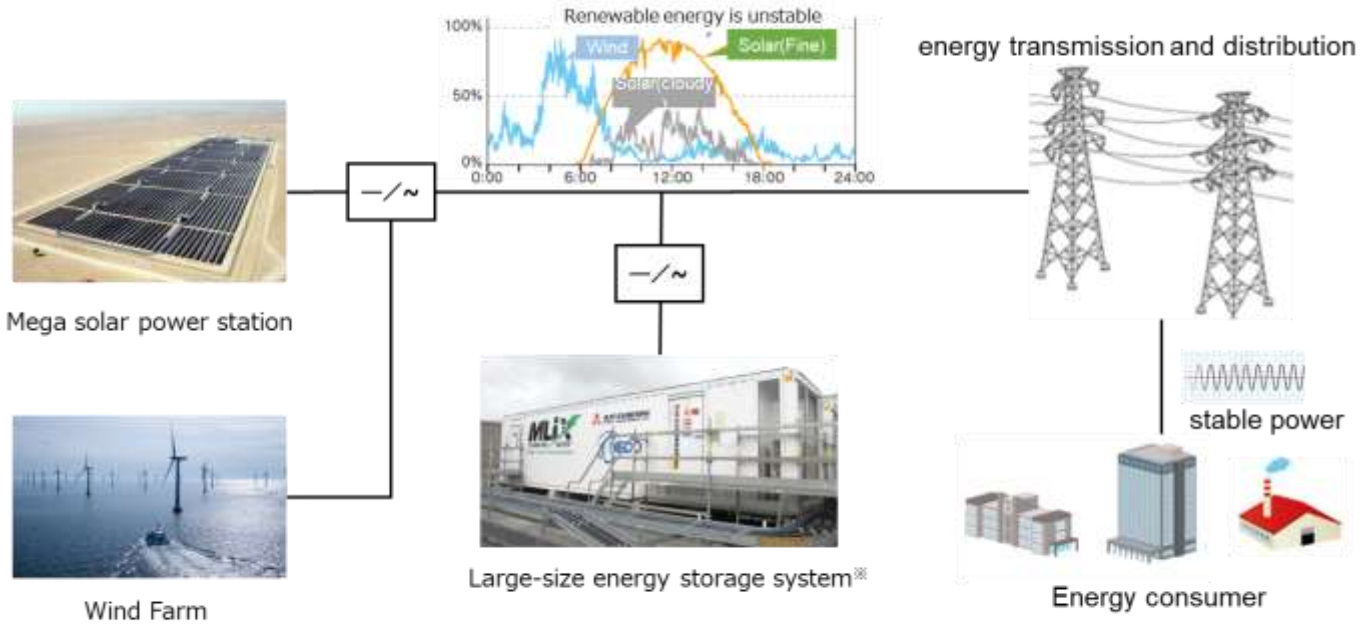


Fig. Grid connection facilitation system using power storage system

Wide Temperature Operation

- Operation temperature of LIB: 0 °C ~ 45 °C
- Low temperature: Safety problem, Li metal deposition on anode side, Charging problem
- High temperature: Short life, Electrolyte problem, Safety problem
- New electrolyte system is required to solve these problems.
- New materials are also required for next generation LIB.

High Quality Production

- Safety of LIB strongly depends on production control.
- Japanese battery companies have a lot of experiences for quality control of LIB.
  - Humidity control, Foreign body inspection, Precise cell manufacturing
- Japanese material companies can provide high quality materials for LIB, leading to both high performance and safety of LIB.
  - Cathode active Materials, anode active materials, electrolytes, separators, binders, conductive materials, cell package and so on.
  - All materials can be produced in Japan with highly precise control.
- High quality production = high performance and high safety.

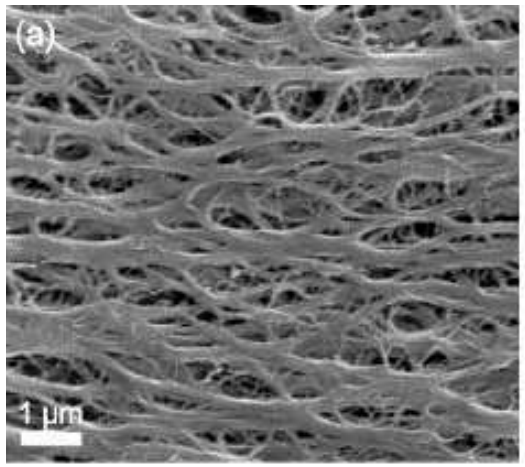
Research Fundings for LIB in Japan

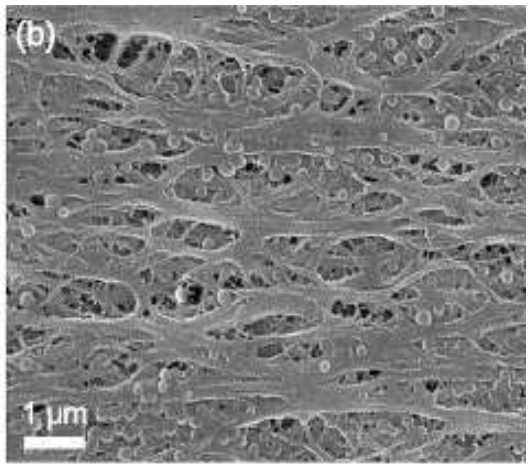
- GteX, Japan Science & Technology, LIB and Next Generation Batteries
- COI-NEXT, Japan Science & Technology, Battery & Material Research, Platform for battery research and development
- Rising 3, NEDO, Fluoride battery, Zn battery
- SOLiD-NEXT, NEDO, All solid state battery
- GteX project includes next generation LIB development.
- Material research and Cell base research are included in GteX project.

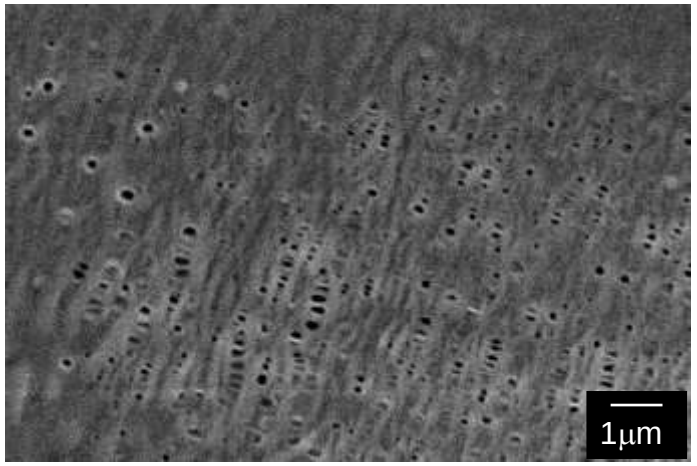
Next Generation LIB

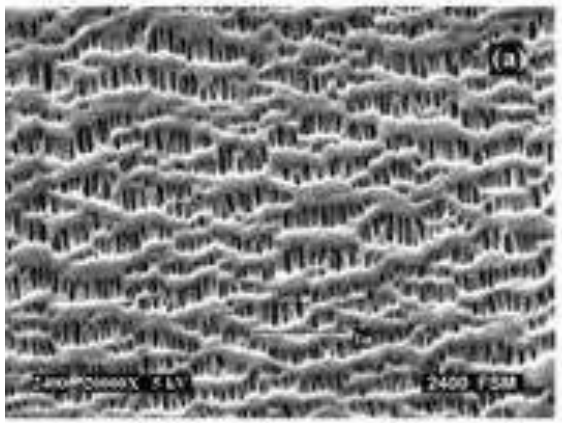
- Long cycle life
- Operation under wide temperature
- Low cost
- High safety
- High energy density
  - Including Li metal battery
- New materials are required.
  - Active materials, Binders, Conductive additives, Electrolyte, Separator and so on.
- New type separator: 3DOM separator

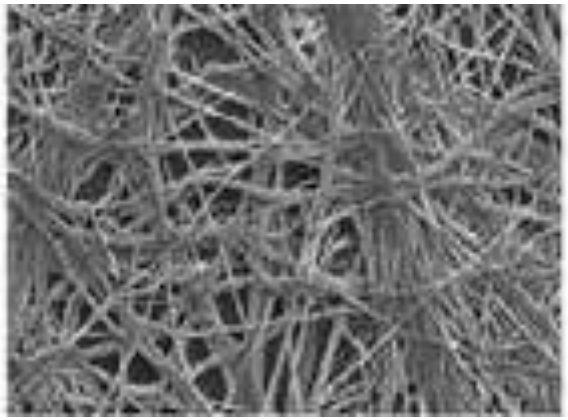
SEM of Separators







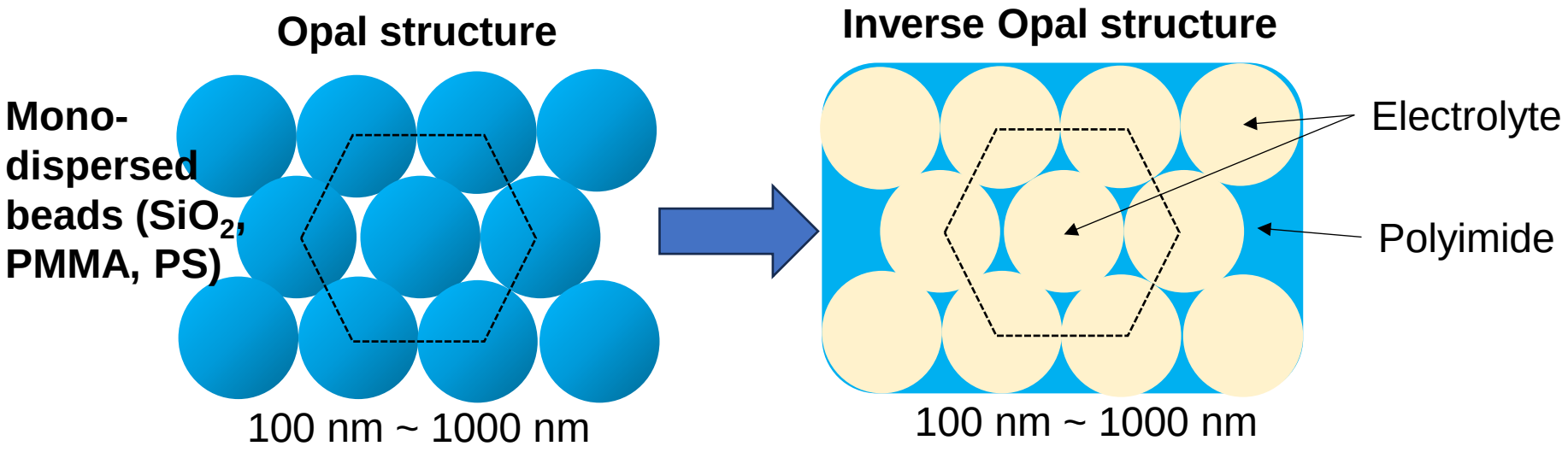




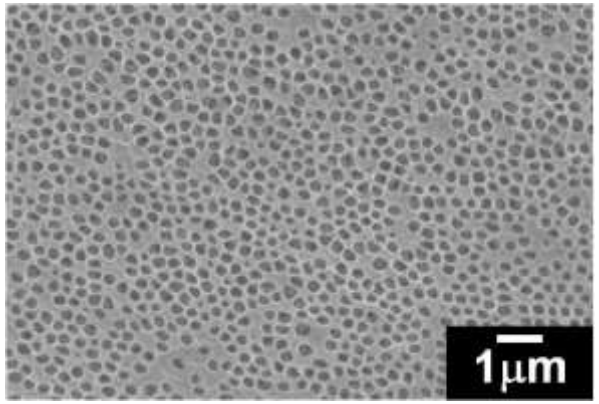
Each separator has a different porous structure. Pore distribution is not so uniform, leading to large current distribution.

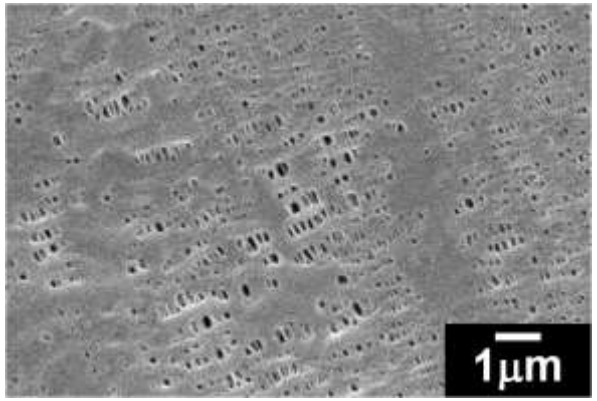
3DOM Separator

- Regular structure for high porosity separator
- Three dimensionally ordered microporous (3DOM) structure is one of useful porous structure. (Inverse opal structure)



Properties of PP & 3DOM-PI

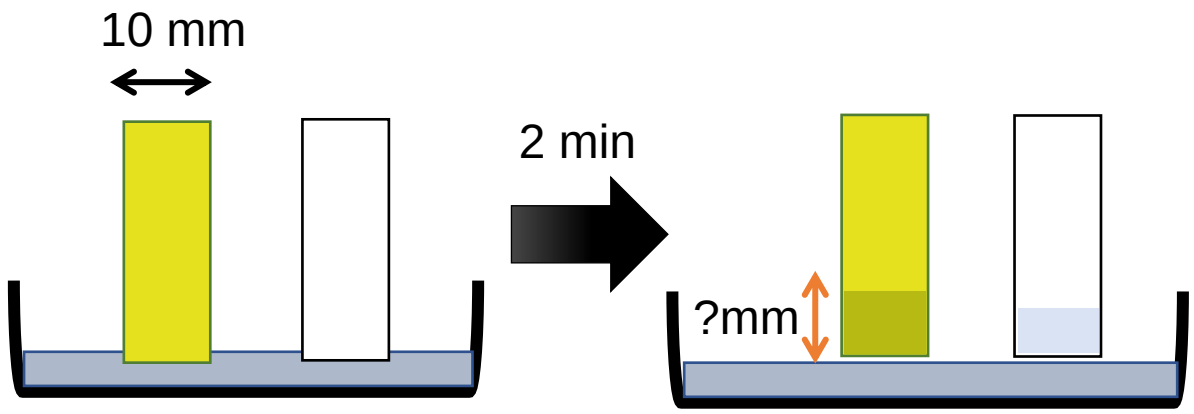


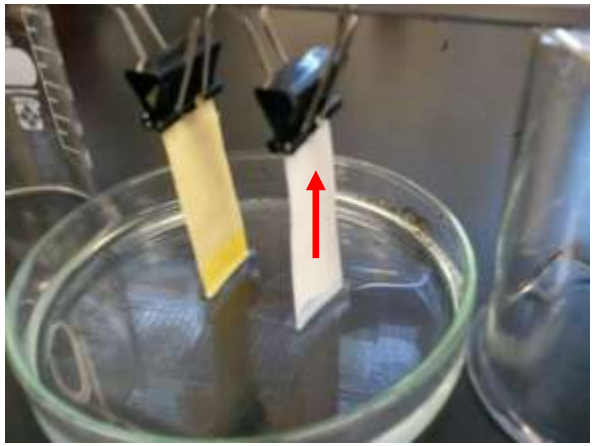


The pore size and thickness of 3DOM PI separator are controlable.

	3DOM PI	Conventional PP
Porosity	≒ 70 %	≒ 40 %
Pore size	≒ 300 nm (controllable)	Random
Thickness	15 μm (controllable)	10 μm
Gurley (JIS)	32 sec	620 sec

Affinity to Electrolytes





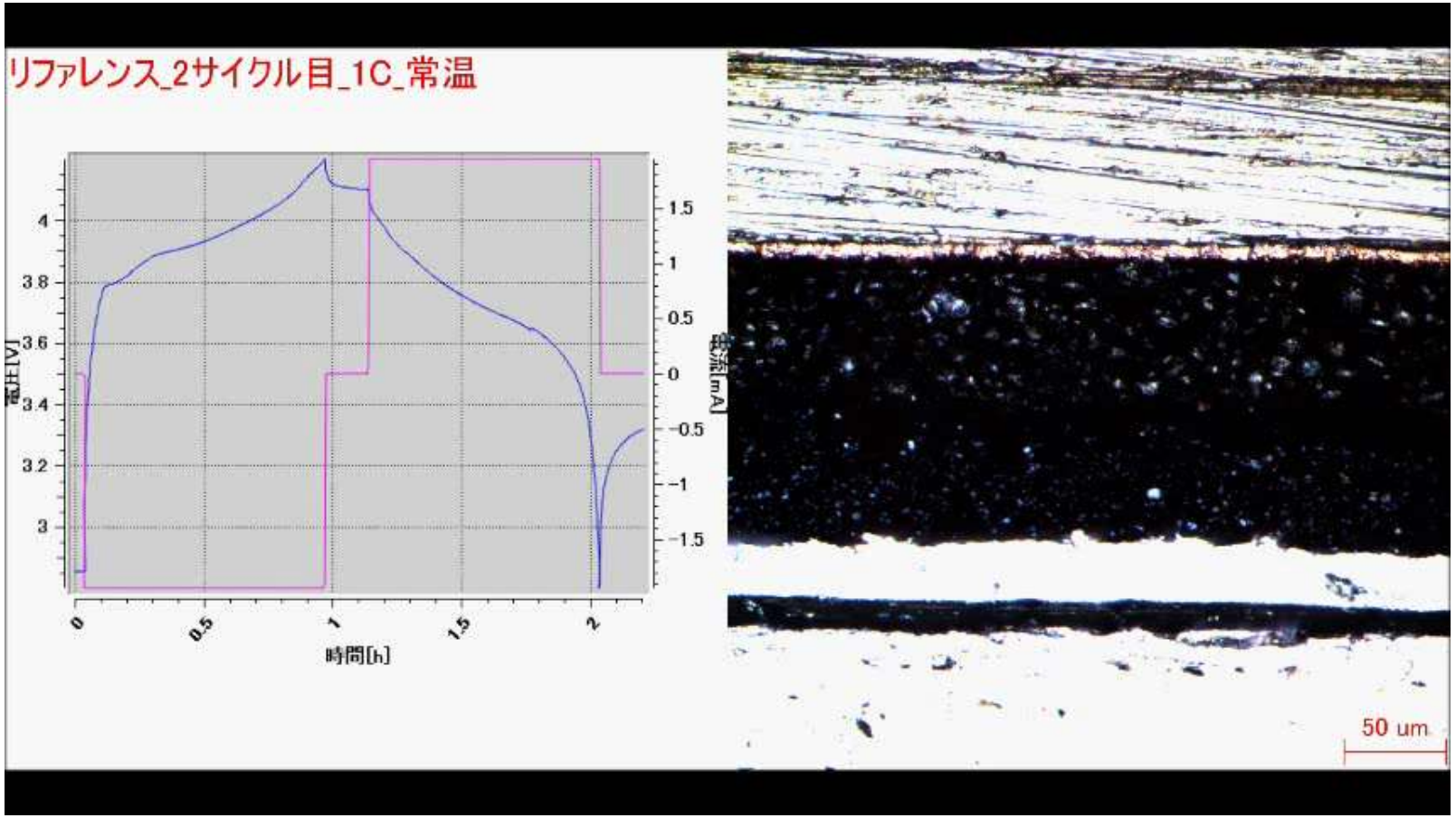
Electrolyte solution	3DOM PI separator	Conventional PP separator
1 mol dm^{-3} $LiPF_6$ in EC : DEC = 1 : 1 (in vol.)	8.0 mm	4.0 mm
1 mol dm^{-3} $LiPF_6$ in EC	7.0 mm	x

3DOM PI separator has high affinity to electrolyte solutions due to highly hydrophilic property.

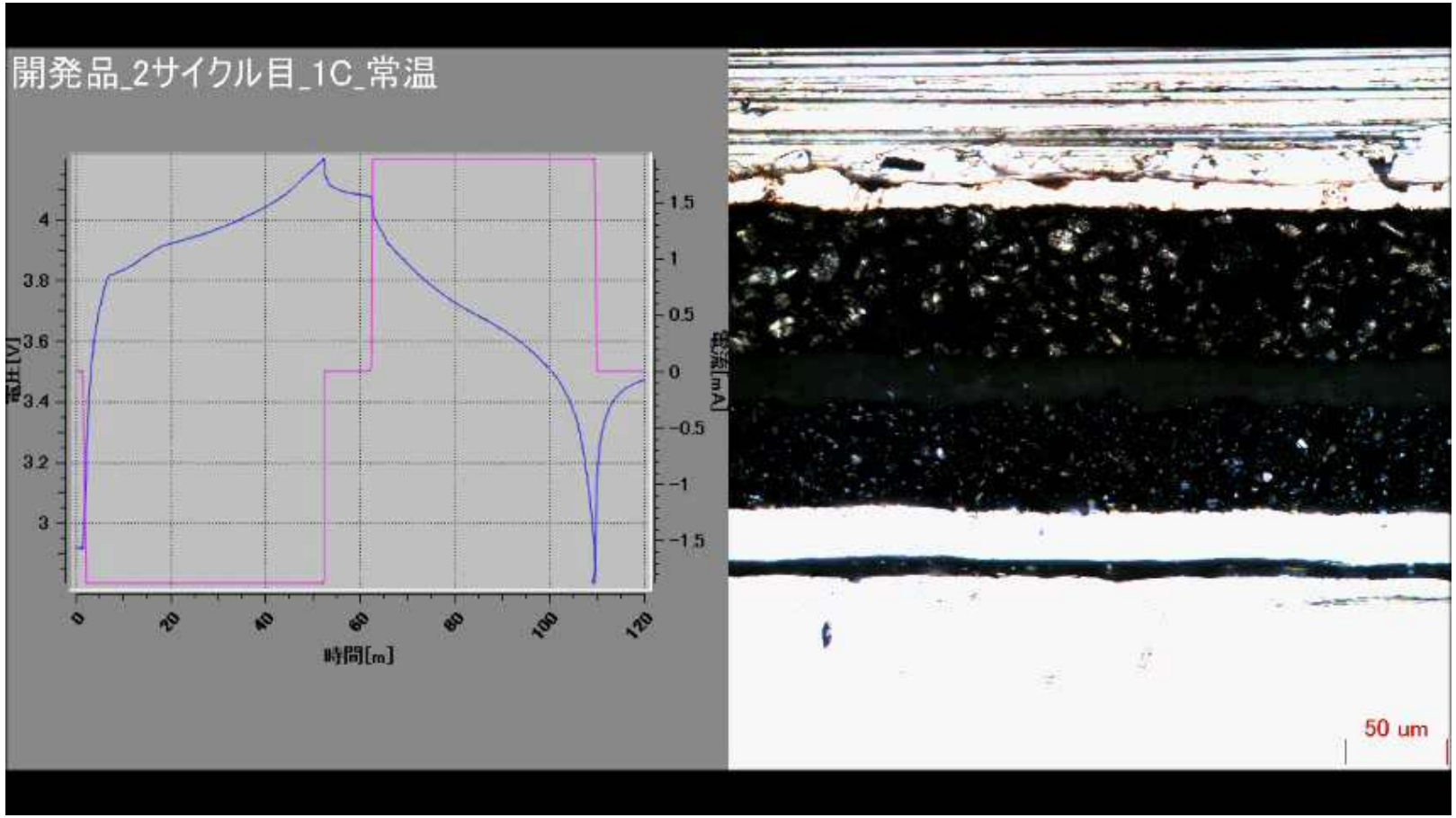
Wettability of Electrolyte to Separator

- 3DOM-PI separator can take up all of electrolytes, even electrolyte with high viscosity, such as highly concentrated electrolyte and ionic liquid which can not be applied to cell with poly-olefin separator.
- Long cycle life and high temperature operation of LIB are strongly dependent on a kind of electrolyte.
- 3DOM-PI separator can enable to use the best electrolyte for long cycle life and high temperature operation of LIB.
- For example, EC+PC/LiFSI electrolyte usually can not be utilized in LIB.
- EC+PC/LiFSI is stable electrolyte even at 150 ^{o}C. This electrolyte has been applied to LIB.

For long Cycle life of LIB



For long Cycle life of LIB



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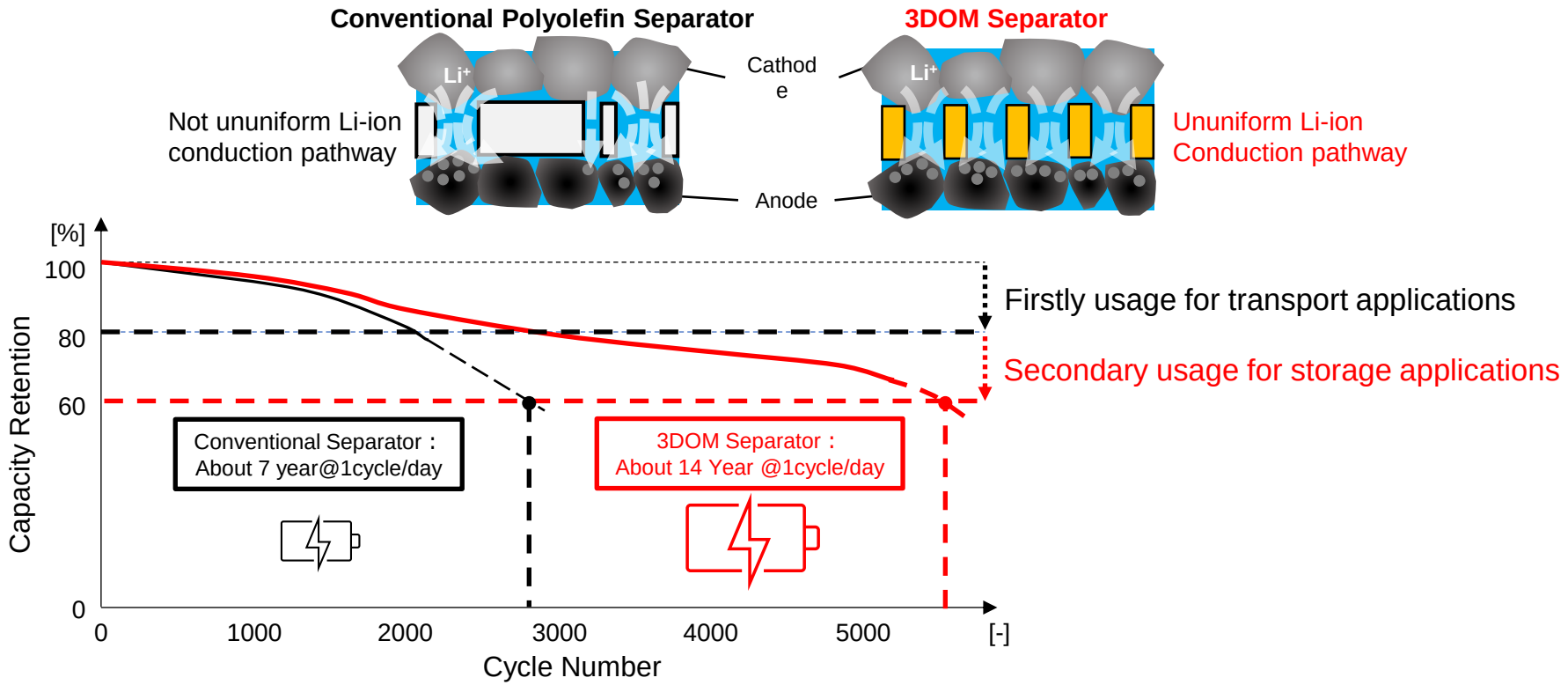
Cycle Performance of LIB

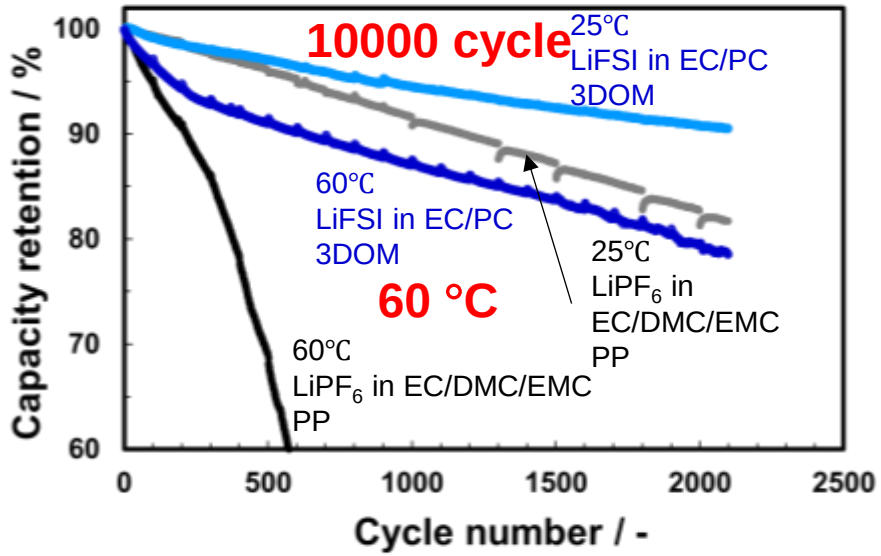


The cycle life performance of the cell with 3DOM separator is two times compared to the one with polyolefin separator at EOL 60% due to uniform Li-ion conduction pathway. Therefore, the cell with 3DOM separator can brings considering stable secondary usage for storage applications.

Cyclability of LIB at High Temperature

Cell configuration: NCM523/Separator with LiFSI in EC/PC +VC+PS/Graphite

Electrode	Cathode(NMC532, AB, PVdF) Anode(Graphite, PVdF)
Separator	3DOM separator (Porosity:56%, Thickness:20μm) Polyolefin separator (Porosity:40%, Thickness:20μm)
Electrolyte	LiFSI in EC/PC +VC+PS $LiPF_6$ in EC/DMC/EMC+VC+PS
Operating voltage / V	2.8-4.2 Charge:1C-CCCV(0.05C cut off) Discharge:1C-CC
Cell capacity / mAh	26



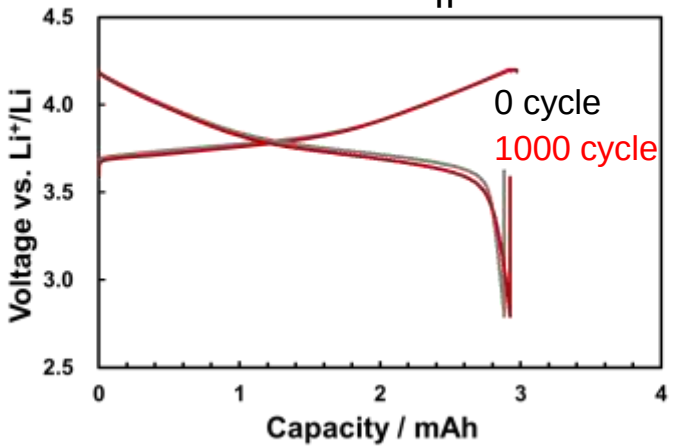
1C discharge capacity@1cycle = 100%

The discharge capacity was maintained during 2000 cycles (Cut off Capacity: 80%) at 60 °C.

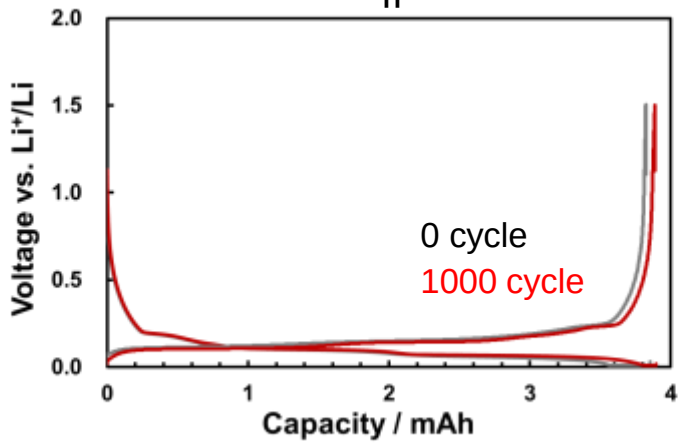
Degradation of Cathode and Anode in LIB

After 60℃, 1000 cycle
【LiFSI in EC/PC with 3DOM separator】 → NMC532||Li
Gr||Li

Cathode
NMC532||Li



Anode
Gr||Li



Cell

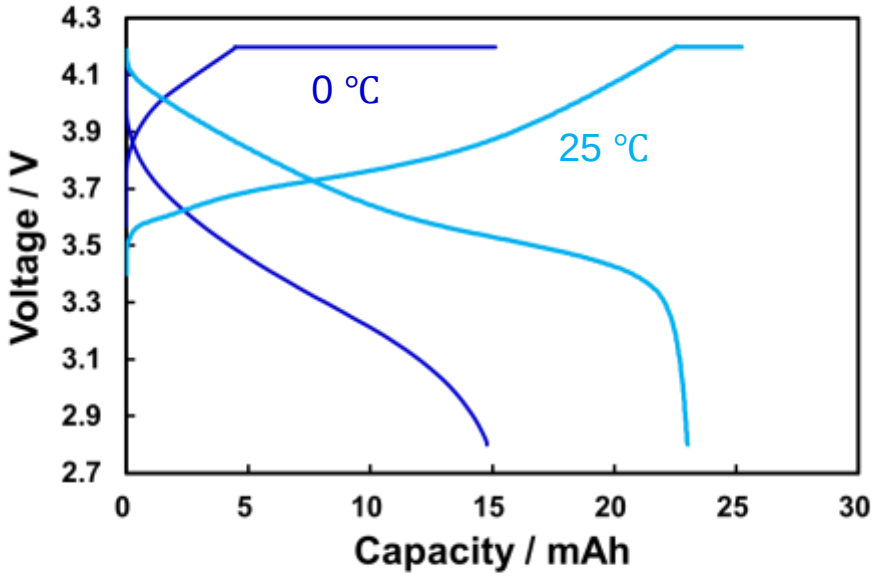
Separator	Polyolefin separator (Porosity:40%, Thickness:20μm)
Electrolyte	$LiPF_6$ in EC/DMC/EMC +VC+PS
Cell size / mm	Φ14 (coin)

Both cathode and anode exhibited no degradation.
The capacity fading may depend on a stability of electrolyte.

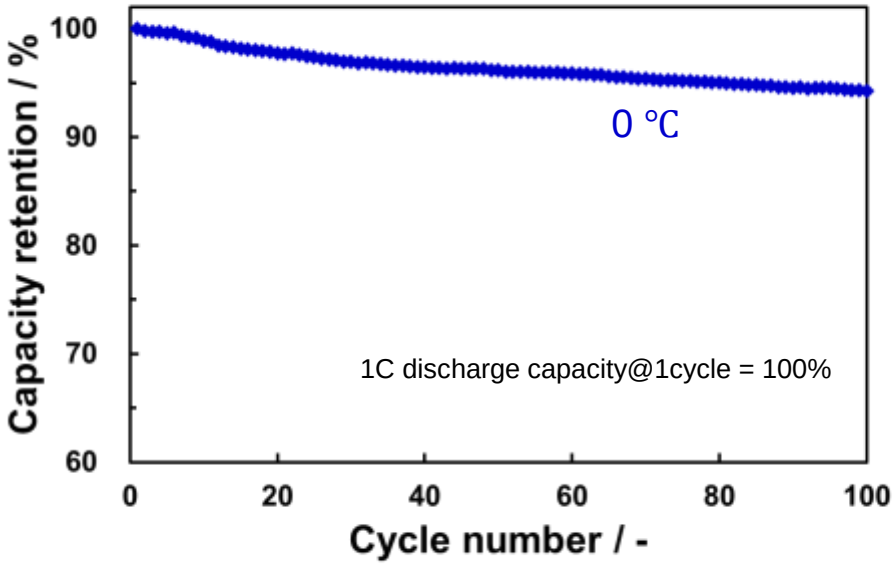
Cycle Performance of LIB at 0 °C

【Electrolyte (LiFSI in EC/PC) Cathode (NMC532) Anode (Graphite)】

Discharge and charge curves at the first cycle (1C/1C)

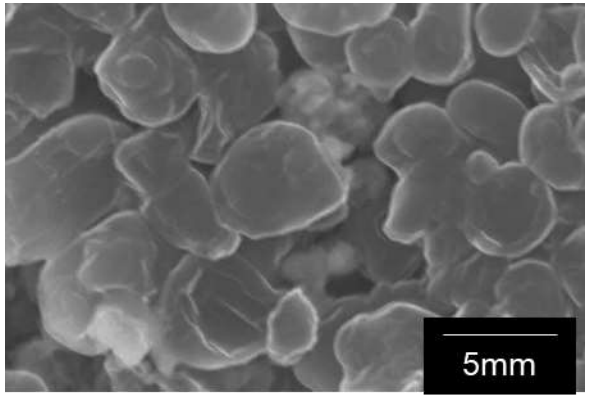


Capacity retention (1C/1C)



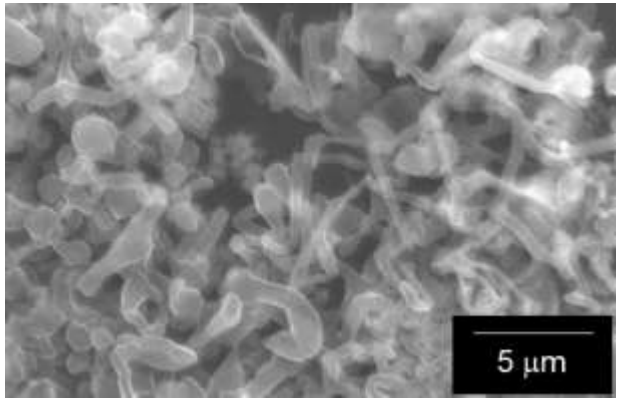
Morphology of Li Metal in Electrolytes

- Morphology of Li metal: granular, dendrite, mossy, etc.
- Surface area (S.A.) of Li metal is a key issue. Larger S.A. leads to more electrolyte decomposition and consumption of Li metal itself.

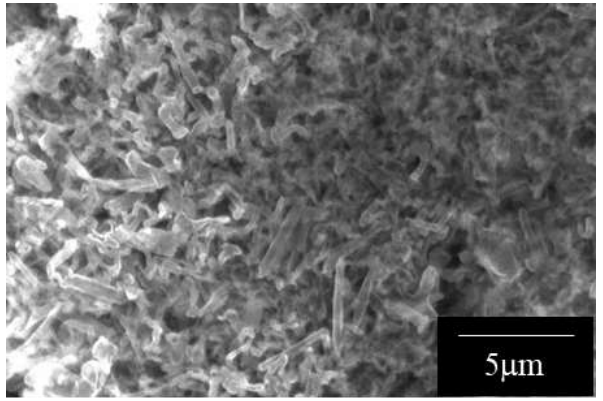


Granular

Good cyclability



Dendrite



Mossy

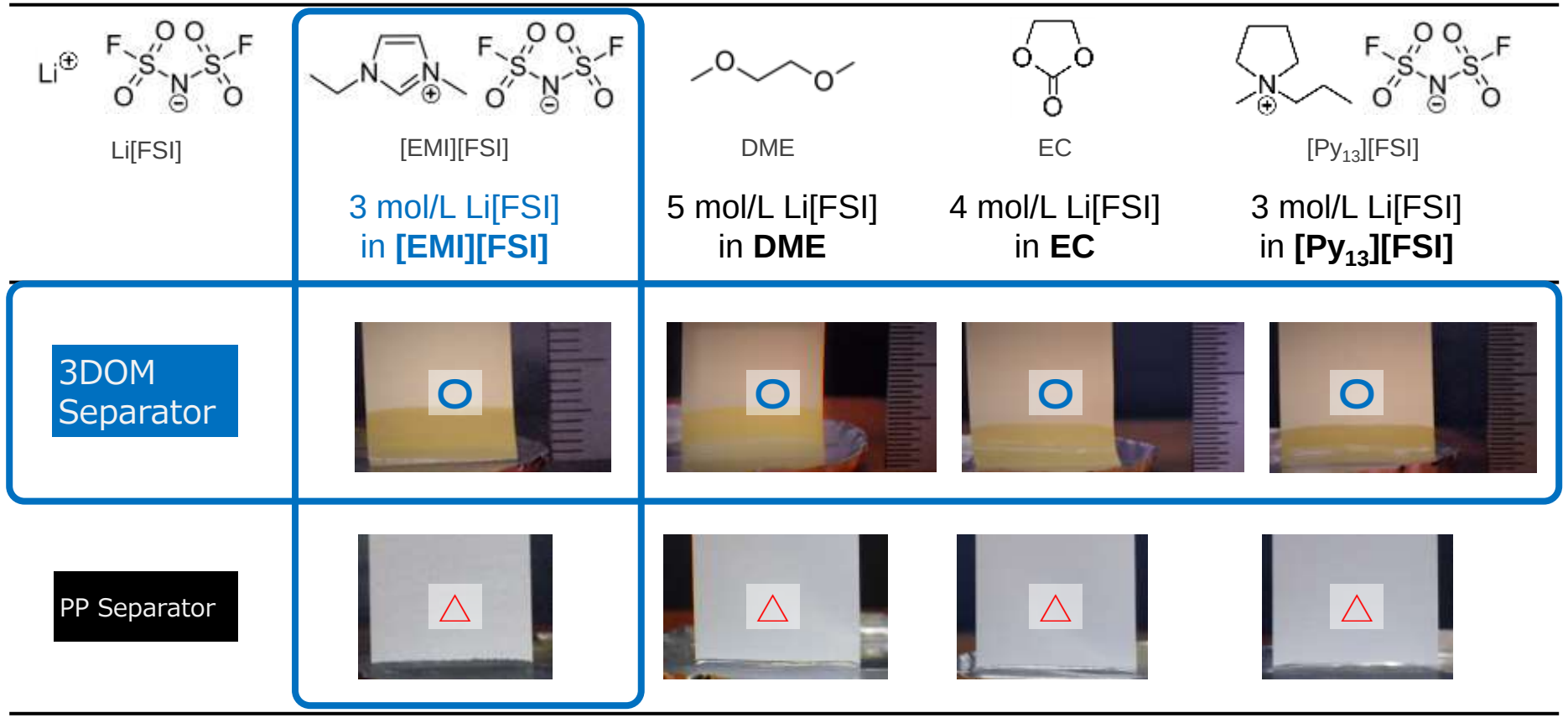
Lower cyclability

Morphology Change of Li Metal with Cycle

Lithium Metal Battery with 3DOM Separator

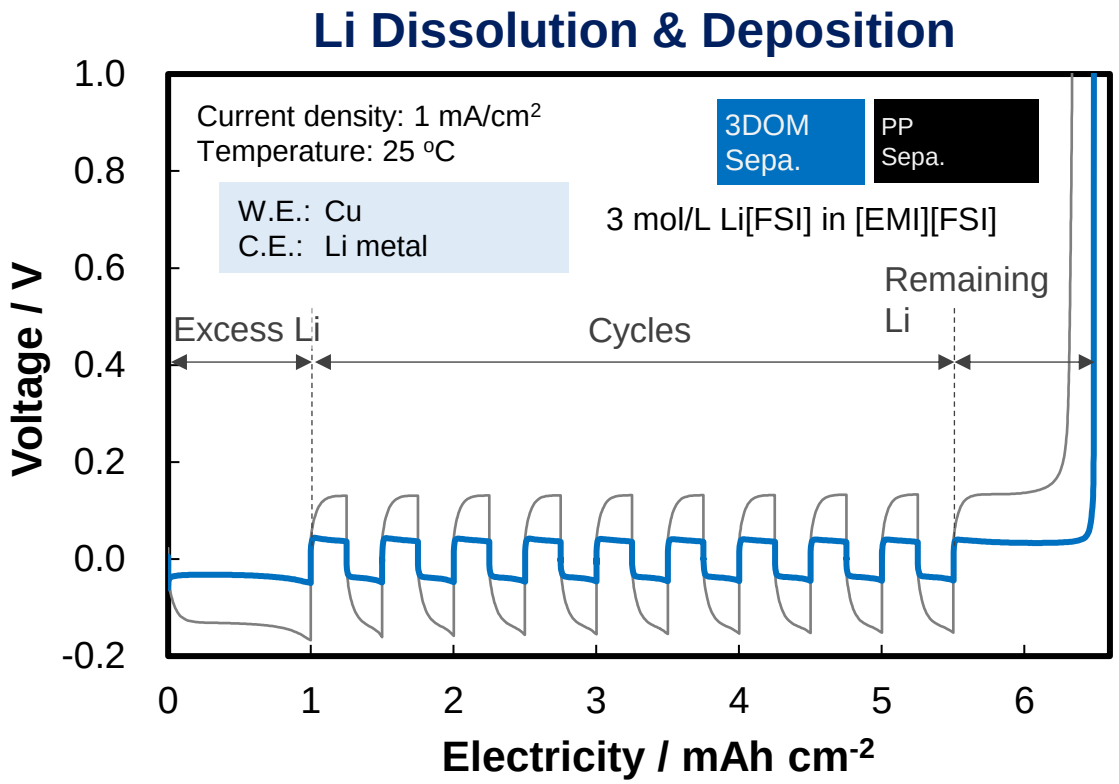
- 3DOM separator suppresses a dendrite formation, due to highly uniform current distribution.
- 3DOM separator provides a highly stable interface between Li metal and separator, due to high mechanical strength of PI.
- An amount of electrolyte contained in 3DOM PI separator is larger than that in poly-olefin separator, due to high porosity and capillary force.
- In this study, highly viscous ionic liquid electrolyte was used to suppress chemical reaction between electrolyte and lithium metal.
- NMC/Li full cell was fabricated using 3DOM PI separator and ionic liquid or gel electrolyte.

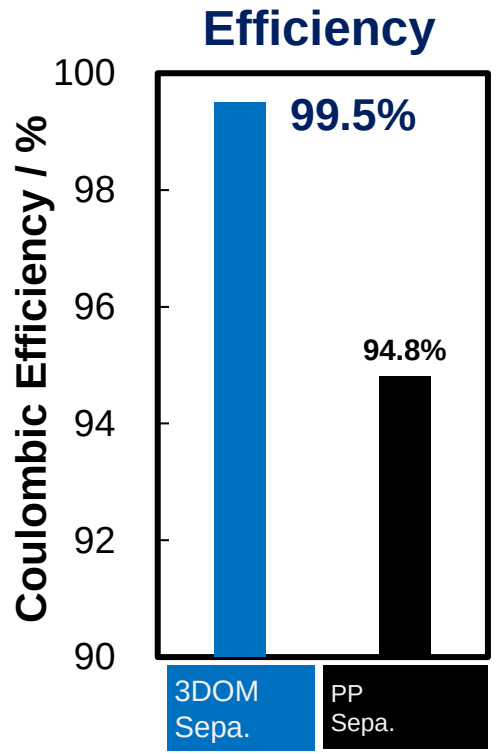
Affinity of Electrolyte for LMB



After 3 hours

Coulombic Efficiency of Li Anode for LMB





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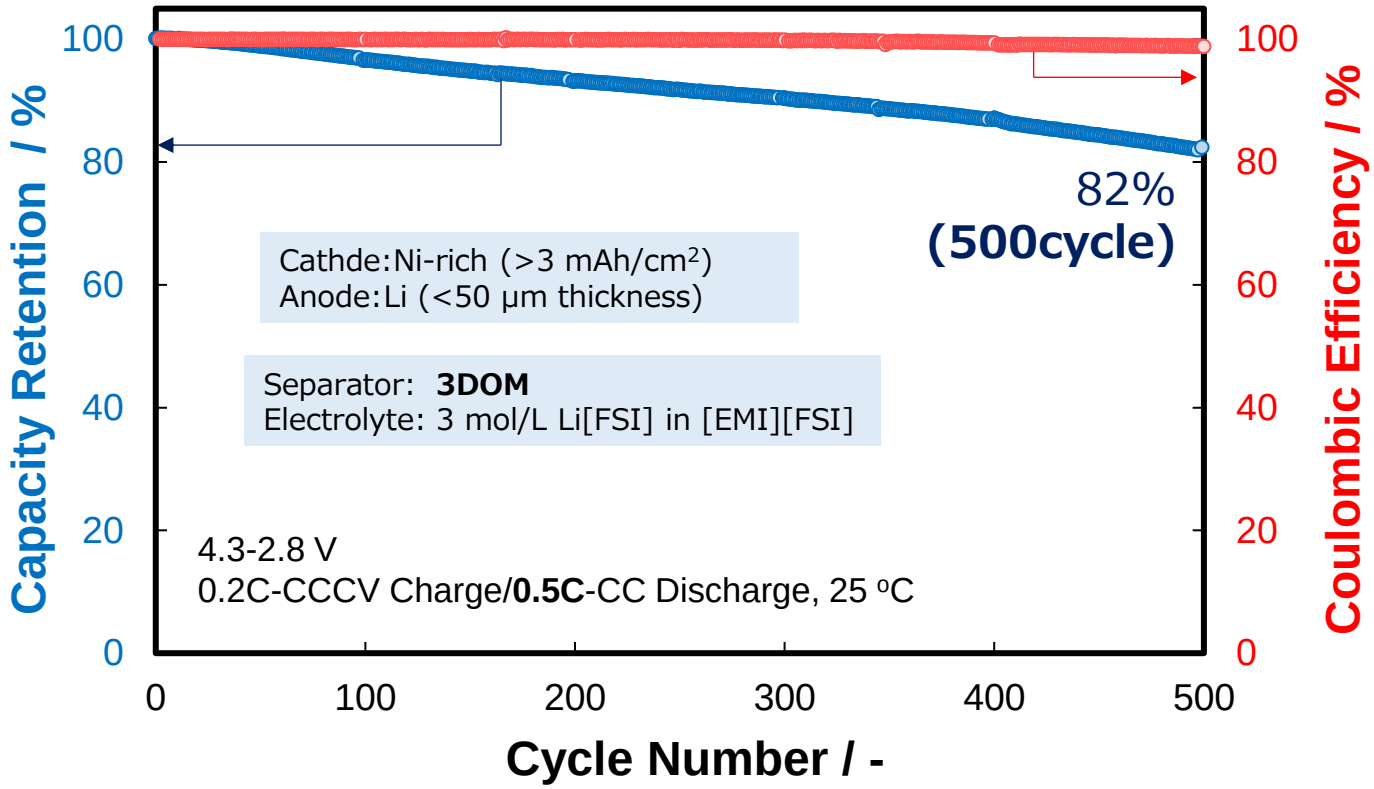
Cycle Test of LMB (40 mAh)



Summary

- Performance which is required for new LIBs is made clear from Life Cycle Assessment of CO_2 emission.
- Japanese material and cell assembling for LIB are superior, contributing safety and cycle life of LIB.
- New LIBs are developed in GteX project in Japan.
- For example, 3DOM separator was introduced.
- 3DOM separator contributes long cycle life of LIB, stable operation of LIB in wide temperature range, and utilization of Li metal anode.